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(54) CONSTRUCTIONAL CEMENT

(71) We, THE ASSOCIATED PORTLAND CEMENT MANUFACTURERS LIMITED, a Company organised under the laws of Great Britain, of Portland House, Stag Place, London SW1E 5BJ, England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to constructional cements and more particularly to a cement composition to fulfil the same role as Portland cement or high alumina cement, especially in applications where these two latter cements are not suitable.

Portland and high alumina cements, by virtue of their compositions, depend for their setting and hardening upon the formation of calcium hydroxide and hydrated silicates and aluminates in the case of Portland cement, and hydrated aluminates in the case of high alumina cement. A characteristic of both these cements is that the set products are more or less alkaline, i.e., the pH is above 7.

As is well known, these products are not completely resistant to attack by many sulphates, especially in high concentrations, or by certain salts of bases, such as magnesia (e.g., magnesium sulphate and magnesium chloride) in the case of Portland cement and sodium in the case of high alumina cement, which latter is also subject to deterioration in time at both normal and elevated temperatures. The hydrated products of both these cements are slightly soluble in water, particularly in water of low hardness value. Neither of these cements is resistant to solutions of mineral or organic acids in practically any significant concentration due to the alkaline nature of the hydrated cement products. It has been claimed that high alumina cement is resistant to acid solutions of pH 4 or greater. This degree of acidity is, however, very low.

Both Portland and high alumina cements are attacked by sugar solutions.

Because of the alkaline nature of these cements when mixed with water they are not permanently compatible with glass fibre or silica fibre because they attack these materials chemically especially at the surface which contributes most of their strength. Recently a special glass with a higher resistance to alkaline attack has been developed by the former Building Research Station but it is significantly more expensive than the usual fibre glass.

The very high strength silica fibre cannot be used with these cements. The result is that this form of reinforcement is mostly confined to the use of glass fibre with plastics materials such as epoxy and polystyrene resins, which are not fireproof.

The present invention overcomes these disadvantages by relying on a completely different chemical reaction in the setting cement. It relies on the reaction of a selected artificially prepared chemical combination of mineral oxides with a solution of orthophosphoric acid, to form metal phosphates which set to a hard mass.

According to the present invention we provide a method of making a constructional cement which comprises (a) preparing a particulate chemical combination of oxides selected from (i) anorthite with excess silica in solid solution in the anorthite and (ii) anorthite with albite in an amount not more than 30 per cent by weight in solid solution in the anorthite, by sintering a mixture of minerals which together contribute the constituent oxides of the combination or of compounds which form said oxides under sintering conditions, in stoichiometric proportions to form said combination, whereby said oxides combine, and grinding the sintered product; and (b) reacting said ground product with an aqueous solution of orthophosphoric acid.

The invention further provides a concrete or mortar or other composite product produced by mixing said combination of oxides with the orthophosphoric acid solution and an inert aggregate or a fibre reinforcement.

The composition of the orthophosphoric acid solution should preferably be within the following range:—

| | | |
|---|--------------------------|--------------------------------------|
| 5 | orthophosphoric acid | 35 per cent to 75 per cent by weight |
| | zinc orthophosphate | 0 per cent to 15 per cent by weight |
| | aluminium orthophosphate | 0 per cent to 20 per cent by weight |
| | water made up to | 100 per cent. |

In all the tests and Examples referred to herein, a phosphoric acid solution was used which has the following composition:

| | | |
|----|----------------------|-----------------------|
| 10 | orthophosphoric acid | 38 per cent by weight |
| | zinc orthophosphate | 14 per cent by weight |
| | water to | 100 per cent. |

More specifically the cementitious composition is produced by calcining a mixture which contains or forms CaO , SiO_2 and Al_2O_3 with other possible oxides, these oxides being present mostly in compounds or being formed under the reaction conditions, in the proportions required.

Material contained or formed in said mixture, extraneous to the requirements for producing the said combinations of oxides, and inactive in the formation of a cement according to the invention, are referred to herein simply as inactive, or inert, materials.

Suitable raw materials for the artificially prepared combinations of oxides include clays, marls or clay-like materials or materials derived therefrom, examples being London clay, Kimmeridge clay, Oxford clay, china clay, shales and slates, and coal ash or pulverised clinker. These by themselves may not be of suitable composition and require the addition of alumina, calcium carbonate, limestone, silica sand or even other clays or materials containing substantial amounts of one or other of these substances.

For constructional use it is of advantage to use compositions providing a significant amount of iron oxide as the resulting cements develop greater strength. When naturally occurring ferruginous clays, such as London clay, are used the cost of the raw materials will be less. Cements low in iron oxide, based on china clay, are useful if a white, light coloured or refractory cement is desired.

The raw materials are mixed together and finely ground, preferably wet, in ball or tube mills. It is of advantage to grind the raw materials to the finest degree that is economically advisable. If they are sufficiently soft they may be ground in wash mills or tumbling drums and, if necessary, ground further in ball or tube mills. They are calcined preferably in rotary kilns such as those in Portland cement manufacture or other convenient furnaces according to circumstances. Such convenient furnaces may be kilns of the type used for firing building or refractory bricks which can be very economical especially if certain fuel-containing clays, such as Oxford clay, are used.

The optimum temperature of calcination for the artificially prepared cements is that which produces substantially complete chemical combination as determined by known chemical methods and which, for a given fineness of grinding of the cement, gives the highest strength in the final concrete. The temperature of calcination is within the sintering range and will depend upon the composition and is determined by trial. For instance, with London clay, bauxite and chalk the calcination temperature may be as low as 1100°C , whereas with china clay and chalk it may be as high as 1500°C . Temperatures of firing thus lie generally between 1100°C and 1500°C but are not contravened by firing at somewhat higher temperatures depending upon the raw materials used.

Although the firing would normally be carried out in an oxidising atmosphere it is of no disadvantage to fire in a reducing atmosphere. In the application of the invention reaction of anorthite with the orthophosphoric acid forms calcium phosphate and aluminium phosphate and, if iron oxide is present in the raw materials, ferric or ferrous phosphates, which set to a hard mass. If the calcination temperature is above 1216°C some or all of any monocalcium ferrite present is decomposed and some ferric oxide with possibly some ferrous oxide is formed. If the calcination takes place in a reducing atmosphere ferrous oxide is formed and at higher proportions of iron oxide, e.g., above an equivalent of about 15 per cent Fe_2O_3 , ferrous oxide will be formed even in an oxidising atmosphere. Ferrous oxide reacts with phosphoric acid to form ferrous phosphate which contributes to the strength of the product. In these cements the ferrous oxide, when present, usually occurs with ferric oxide as magnetite. Magnetite, whether artificial or natural, when ground, reacts with orthophosphoric acid solutions to give a cement which sets and hardens giving a high strength. However, unless ground very coarsely it is quick or flash setting.

In relation to the calcination, it should be understood that sintering involves the production of a certain amount of melted material but the mass is not fluid at the maximum

temperature although it may be in a plastic state which helps in the formation of nodules if the heating is in a rotary kiln.

Compositions intended for making anorthite but containing much excess silica, e.g., above 10 per cent, are usually deleteriously affected by melting and especially quenching, which steps produce a glass containing no anorthite, during reaction with orthophosphoric acid excessive silica is liberated in a gelatinous condition which weakens the eventual concrete. An example is a cement having the composition: SiO_2 52.3 per cent; Al_2O_3 30.1 per cent; Fe_2O_3 0.7 per cent; CaO 16.8 per cent which had been melted and quenched in water; it was a glass containing no anorthite. This gave a cement, which, when mixed neat with the phosphoric acid solution, set slowly and eventually hardened to a moderate degree. When made into a concrete it still had no significant strength at 8 months. The same composition when prepared by sintering gave a concrete with a normal setting time and which hardened satisfactorily giving in the 1-inch concrete cube test a strength of 6500 p.s.i. at one month. This cement contained 82 per cent anorthite, 16.9 per cent excess silica and 1.1 per cent minor oxides. When sintered and not quenched, less silica is liberated in a gelatinous condition. Thus the method employed in accordance with the invention is sintering.

The calcination temperatures can be reduced significantly by the use of fluxes. If the iron oxide content exceeds 10 per cent by weight it is preferable, to avoid dissociation of monocalcium ferrite, that the firing temperature does not exceed 1200°C and the addition of a flux may be advisable if good combination is not attained. Provided economic and atmospheric pollution factors permit, the use of fluxes is of considerable advantage. Some raw materials, such as ordinary clays (London clay is an example), already contain fluxes in the form of alkalis but can be improved by the addition of further fluxes, possibly of a different type.

Fluxes that are of value are the alkalis, fluorides such as fluorspar (or calcium fluoride) and natural or artificial cryolite, and sodium or potassium fluoride.

Alkali fluxes should be limited in use as they may lead to soluble compounds on reaction with phosphoric acid. Amounts up to 5 per cent by weight Na_2O plus K_2O are safe. If more flux is desired it is better to introduce fluorspar or cryolite.

Cryolite is the most powerful of all the fluxes and if economic and pollution factors permit it is the one to choose but it contains an alkali (sodium) and, therefore, should be used with care. Fluorspar is free from this disadvantage, is cheaper but is less powerful. All the mixtures considered in this application are improved in one way or another by the

careful addition of fluxes. This is particularly the case with the low iron oxide or iron free mixtures. These mixtures would be used for making a white and/or refractory cement but fluxes may be contra-indicated here as they may spoil the colour and will reduce the refractory property.

The setting time and rate of hardening of the cement is very flexible and is governed largely by its composition, fineness and the composition of the solution of phosphoric acid. These factors are decided by trial according to the properties required. The setting time may thus be adjusted by employing at least two said combinations of oxides having different individual cement-setting rates. Alternatively or in addition, the combination of oxides may be augmented by a compound having a retarding effect on the setting of the cement. Such a compound may be added in the artificial preparation of a combination, or may be present in the raw material, in either event as a chemically separate ingredient or combined with the other oxides.

Setting time is controlled to some extent by the amount of water in the orthophosphoric acid solution, and some degree of increase of setting time is brought about by increasing the concentration of orthophosphoric acid. Temperature also has an effect; low temperatures increase the setting time, higher temperatures decrease it.

For the purposes of this invention the fineness of the cements is characterised by its characteristic particle size (C.P.S.). The characteristic particle size is the particle size below which there is 50 per cent by weight of the cement and is determined by the well-known Andreasen Sedimentation Method (British Standard 3406; Part 3: 1963, "Methods for the Determination of Particle Size of Powders. Liquid Sedimentation Methods").

Anorthite by itself gives a cement with an extremely quick setting rate unless very coarsely ground; it is necessary to moderate its action. It was found that incorporating an excess of silica in the raw mix produces a retardation of the setting time. This occurs through solid solution of some of the excess silica in the anorthite. An excess of alumina enhances the retardation by excess silica but excess alumina by itself is a poor retarder.

In the research work done by Rankin, Wright and others in the United States of America, in investigations of the Ternary System $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, no solid solutions were found between anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and silica or alumina. This is because of the way the experiments were made. The samples were first melted and then cooled to various temperatures and quenched, or were melted and then very slowly cooled to obtain equilibrium. If the

compositions are not melted but sintered a different state of affairs is obtained and solid solutions of silica, or silica and alumina, with anorthite are obtained. We have shown this by optical measurements in microscopical investigations. The presence of anorthite in the sintered specimens has been proved by microscopical methods and by X-ray diffraction analysis. X-ray diffraction shows that in melted and quenched samples (glasses) anorthite is absent.

Merely mixing finely ground silica and/or alumina with anorthite does not increase the setting time beyond the small amount caused by increasing the liquid/anorthite ratio due to dilution of the anorthite with the silica. The mixture remains very quick setting as before.

A series of four cements was made to demonstrate the effect of solid solution.

Cement A

This cement consisted substantially of anorthite in the crystalline state and was made by sintering a mixture of 71.8 per cent by weight china clay, 3.1 per cent by weight alumina and 25.1 per cent by weight calcium carbonate at an average temperature of 1460°C for 10 minutes giving a thoroughly sintered and combined product. (The melting temperature of anorthite is 1553°C). It was confirmed by microscopical examination that the product consisted of anorthite crystals between 1 and 5 microns equivalent diameter and proved to be anorthite by X-ray diffraction analysis.

The product was ground to a C.P.S. of 11.9 microns. When mixed with the phosphoric acid solution it set instantaneously, with generation of heat and was quite unworkable.

Cements B to E

This was a series of four cements constituted to consist of anorthite and gradually increased amounts of excess silica. The mixes were sintered with the excess silica in them i.e., the excess silica was not mixed with the cement.

The results were as follows:

| Cement | Per cent by weight excess silica | Relative setting time mins. | |
|--------|----------------------------------|-----------------------------|----|
| B | 5 | 12 | 50 |
| C | 10 | 15 | |
| D | 15 | 22 | |
| E | 20 | 42 | 55 |

When pure anorthite cement is merely mixed with finely ground silica the mixture behaves quite differently from the above cements B to E. For instance, a mixture of 40 per cent by weight pure anorthite and 60 per cent by weight finely ground quartz (C.P.S. 6.8 microns) remained 'flash' setting with the phosphoric acid solution and could not be worked. The same was the case with other orthophosphoric acid mixtures within the range referred to.

The addition of titanium oxide to the raw mix retards the setting time of anorthite in a manner similar to silica as might be expected but is less preferable on economic grounds. The addition of bone ash (or calcium phosphate) to the raw mix has only a slight retarding action.

It may be seen, therefore, that according to the composition the cement may need to be ground coarsely or finely to give convenient setting times.

Setting time can also be controlled by adjusting the orthophosphoric acid content, e.g., above 50 per cent by weight orthophosphoric acid in the solution the setting time increases with acid concentration, but below this value the effect varies with the composition of the cement. The presence of zinc phosphate or aluminium phosphate in the solution increases the setting time.

Anorthite rarely occurs naturally in the pure state in rocks but in solid solution with the soda feldspar albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) with which it forms a continuous series of solid solution.

The recognised solid solutions have the following names:

| | Name | Per cent by weight Albite | per cent by weight Anorthite |
|-----|-------------|---------------------------|------------------------------|
| 95 | Albite | 100 to 90 | 0 to 10 |
| | Oligoclase | 90 to 70 | 10 to 30 |
| | Andesine | 70 to 50 | 30 to 50 |
| | Labradorite | 50 to 30 | 50 to 70 |
| 100 | Bytownite | 30 to 10 | 70 to 90 |
| | Anorthite | 10 to 0 | 90 to 100 |

Albite is inert as a cement for the purpose of the invention and solid solutions with anorthite reduce the activity of anorthite. For instance, labradorite is substantially inert and so are oligoclase and andesine. Bytownite was prepared and found to make a useful cement

and as the anorthite content was increased the setting time became shorter. The composition albite 30 per cent/anorthite 70 per cent was slow setting and required to be very finely ground. Albite contents greater than this do not make useful cements. Bytownite of the

composition albite 20 per cent/anorthite 80 per cent gave a useful cement with an initial setting time of 25 minutes.

These solid solutions having not more than 30% albite in accordance with the method of the invention are made artificially, the setting time being regulated by the amount of albite in solid solution but regulation by excess silica is preferred as more convenient as described above.

In general the cements used in the present invention may be ground in a dry state but they are preferably ground wet. The latter usually has the effect of increasing the setting time for a given rate of hardening. At the same C.P.S. the cement has a longer setting time for wet grinding than for dry grinding and it requires more orthophosphoric acid solution for a given consistency which leads to a greater ultimate strength. This behaviour is of great value in the practical use of the cement in constructional projects. If ground wet the product should be magnetized to remove finely divided iron originating from the grinding media which causes bubbling on the addition of phosphoric acid. Magnetizing would not be necessary if ceramic grinding media, with possibly a non-metallic mill lining, are used, or the effect can be much reduced by using hard ferrous alloys. Magnetizing also removes some of any magnetite that may be present and which may have to be replaced as it is a strength-imparting component. In the case where magnetite is the major component wet grinding is contra-indicated and dry grinding or ceramic grinding media with a non-metallic mill lining is advisable.

When the cement is wet-ground the resultant slurry would normally be dewatered but it may also be used wet if an allowance is made for the water present when adding the orthophosphoric acid solution.

As the water content is increased the shrinkage of these cements increases. The turning point between comparatively high and comparatively low shrinkage is at about 54 per cent by weight water; below 40 per cent by weight water the shrinkage is very low. For constructional purposes the cements would normally be used with an aggregate to give concrete. They may, however, also be used with little or no aggregate in combination with glass or silica fibre to form sheet material or members of other shapes with high tensile strength. In this event the lower water content solutions would be used, e.g., 40 per cent by weight or less, to minimise the shrinkage. Manufacture of sheet material would normally be carried out by spraying techniques; special shapes may be made by extrusion.

In an embodiment of the invention, material containing the combination of oxides in appropriately ground form is mixed with gravel and/or sand and then with the solution of orthophosphoric acid, or the material

containing the oxides is mixed first with the acid and then added to the gravel and/or sand. The resulting mixture sets and hardens to a concrete or mortar suitable for constructional purposes. The pH of the setting and hardening products is always below 7. Steel reinforcement, when used, should be pre-treated with orthophosphoric acid before application of the concrete to form a protective layer of the very resistant ferrous phosphate. If this is not done the steel becomes phosphated *in situ* with liberation of hydrogen which weakens its adhesion to the concrete. It is obvious that carbonates must be absent from the aggregates used.

The concretes made with the cement of the present invention are resistant to any sulphate in any concentration, are compatible with glass and silica fibre, and are resistant to sugar solutions and to many dilute organic acids. In powder form, the cements of the invention do not deteriorate in humid atmospheres as do Portland and high alumina cement powders.

EXAMPLES

The following Examples are given for the purpose of illustrating the invention without limiting it thereto. The percentages expressed are by weight.

In the examples given the initial setting time is the time available for mixing the concrete and placing it before it begins to stiffen.

The tests on concrete were made with a 1-inch concrete cube test designed to give the same result as the 4-inch concrete cube test described in British Standard B.S. 12 "Portland Cement". The advantage of this test is that a smaller amount of material is required, less storage space is needed and results with aggressive agents (e.g., sulphates, acids, sugars) are obtained far more quickly. The test was developed by the Research Department, The Associated Portland Cement Manufacturers Limited.

EXAMPLE 1

Raw materials: Tertiary London Clay from Ockenden, in Essex, aluminium oxide, calcium carbonate, sintered at 1150°C.

| Analysis of cement: | per cent | |
|--------------------------------------|----------|-----|
| SiO ₂ | 45.2 | 115 |
| Al ₂ O ₃ | 30.1 | |
| Fe ₂ O ₃ | 6.3 | |
| CaO | 12.8 | |
| MgO | 2.4 | |
| K ₂ O + Na ₂ O | 3.1 | 120 |
| Rest | 0.1 | |
| | 100.0 | |

Characteristic particle size is 10.2 microns.
Compressive strength at one month was 7850

p.s.i. for 1-inch concrete cubes. The phosphoric acid solution used was as defined in the foregoing description. Initial setting time = 30 minutes.

- 5 The presence of iron oxide increases the strength considerably as can be seen by comparing this cement with Example 2 which contains very little iron oxide.

10 There is 32.7 per cent of inert material the analysis of which is:—

| | per cent | per cent based on the cement |
|--------------------------------|--------------|------------------------------|
| SiO ₂ | 51.7 | 16.9 |
| Al ₂ O ₃ | 35.2 | 11.5 |
| Fe ₂ O ₃ | 6.0 | 2.0 |
| CaO | 1.6 | 0.5 |
| K ₂ O | 5.5 | 1.8 |
| | <u>100.0</u> | <u>32.7</u> |

- 20 In the next table the figures from the second column of percentages have been subtracted from the foregoing analysis of the cement, to give the difference (1) which is then recalculated to a basis of 100 per cent (2).

| | (1) per cent | (2) per cent |
|--------------------------------|-----------------|-----------------|
| SiO ₂ | 28.3 | 42.1 |
| Al ₂ O ₃ | 18.6 | 27.6 |
| Fe ₂ O ₃ | 4.3 | 6.4 |
| MgO | 2.4 | 3.6 |
| CaO | 12.3 | 18.3 |
| K ₂ O | 1.3 | 1.9 |
| Rest | 0.1 | 0.1 |
| | | <u>100.0</u> |

- 35 Expressing these percentages in terms of the cement composition the following is obtained:—

| | per cent |
|----------------------------------------------------------------------|--------------|
| CaO . Al ₂ O ₃ . 2SiO ₂ (anorthite) | 50.6 |
| 2MgO . SiO ₂ | 4.2 |
| CaO . SiO ₂ | 1.3 |
| CaO . Fe ₂ O ₃ | 5.8 |
| Excess silica | 4.0 |
| Alkali | 1.3 |
| Inert material | 32.7 |
| 45 Rest | 0.1 |
| | <u>100.0</u> |

EXAMPLE 2

Raw materials: China clay, calcium carbonate. Sintered at 1350°C.

| Analysis of cement: | per cent | |
|--------------------------------|--------------|----|
| SiO ₂ | 47.5 | 50 |
| Al ₂ O ₃ | 38.3 | |
| Fe ₂ O ₃ | 0.7 | |
| CaO | 12.7 | |
| Rest | 0.8 | 55 |
| | <u>100.0</u> | |

The characteristic particle size is 6.1 microns. Compressive strength at one month was 6750 p.s.i. for the 1-inch concrete cube test. The phosphoric acid solution used was as defined in the foregoing description. The initial setting time was 20 minutes.

Treating the figures as for Example 1 the following was obtained:

The inert material was 40.2 per cent of the cement.

Its analysis was:

| | per cent | per cent based on the cement | |
|--------------------------------|--------------|------------------------------|----|
| SiO ₂ | 52.0 | 20.9 | 70 |
| Al ₂ O ₃ | 41.8 | 16.8 | |
| Fe ₂ O ₃ | 1.7 | 0.7 | |
| CaO | 2.5 | 1.0 | |
| Rest | 2.0 | 0.8 | |
| | <u>100.0</u> | <u>40.2</u> | 75 |

In the next table the figures from the second column of percentages have been subtracted from the foregoing analysis of the cement, to give the difference (1) which is then recalculated to a basis of 100 per cent (2).

| | (1) per cent | (2) per cent | |
|--------------------------------|-----------------|-----------------|----|
| SiO ₂ | 26.6 | 44.5 | |
| Al ₂ O ₃ | 21.5 | 36.0 | |
| Fe ₂ O ₃ | 0.0 | 0.0 | 85 |
| CaO | 11.7 | 19.5 | |
| Rest | 0.0 | 0.0 | |
| | | <u>100.0</u> | |

The composition in column (2) is close to that of anorthite, but contains excess silica. The anorthite content of the cement itself is 59.1 per cent.

EXAMPLE 3

This cement was made by grinding an ordinary London Brick Co. Rustic Fletton brick to a C.P.S. of 11.8 microns. These bricks are made by firing Oxford clay to about 1100°C. The strength at three weeks

was 4850 p.s.i. for the 1-inch concrete cube test. The phosphoric acid solution used was as defined in the foregoing description. The initial setting time was 47 minutes.

5 The analysis of the cement was:

| | per cent |
|--------------------------------|-------------------|
| SiO ₂ | 51.3 |
| Al ₂ O ₃ | 21.4 |
| Fe ₂ O ₃ | 6.3 |
| 10 CaO | 10.2 |
| Rest | 10.8 |
| | <hr/> 100.0 <hr/> |

(The Rest consisted of MgO, K₂O, Na₂O, SO₃ and loss on ignition.)

15 In the cement itself there is theoretically 6.8 per cent monocalcium ferrite and about 45 per cent anorthite, excess silica being present in the latter. However, due to the irregular character of the material of the brick these figures should be taken as approximate. The figures correspond to those for material that has been properly homogenised before firing.

25 Fletton bricks usually contain enough lime to behave as a cement when used with orthophosphoric acid. Some stock bricks also behave in a similar manner since they also contain lime.

30 Concretes made with cements of this invention are completely resistant to all sulphates in all concentrations.

35 Except in the case of acetic acid they have, when manufactured and used according to the methods described, a high resistance only to dilute solutions of organic and mineral acids, e.g., of pH down to about 2.5. The cements are completely resistant to acetic acid which actually increases the strength. They are not resistant to lactic acid or caustic soda.

40 Silicate cements having chemical compositions related to some of the cements of the present invention and containing phosphate, are known for dental purposes, see for instance

45 (1) The Science of Dental Materials by E. W. Skinner and R. W. Phillips, published in a sixth edition by W. B. Saunders Company of Philadelphia, U.S.A. and London, U.K., in 1967; and

50 (2) Dental Silicate Cements by A. D. Wilson (U.K.) published as a National Bureau of Standards Special Publication 354 and part of the Proceedings of the 50th Symposium on Dental Materials held October 6/8 1969 at Gaithersburg, Md (U.S.A.) issued June 1972.

60 The Skinner and Phillips book gives the most comprehensive account of the dental silicate cements. All of them are very complex

glasses and are made from highly purified raw materials which, unlike the cements of the present invention, are heated to the molten state and quenched in water and then ground finely. Being glasses they contain no anorthite or crystalline material. 65

In the Bureau of Standards publication the method of manufacture of such dental cements is described: "The powders are unique amongst cements in that they are ground glassy bodies and not crystalline clinkers, a physical state which may account for the translucent nature of the final cement. The dental silicate glass is prepared by fusing a silica and alumina mixture in a fluoride flux containing minor amounts of phosphate. The fluoride flux is based on cryolite; the addition of fluoride lowers its fusion point". 70 75

The cements of the present invention accordingly differ from such dental cements not only by virtue of their quite different nature, scale and purpose, but also in that they contain anorthite or other crystalline compounds and are not glassy. 80 85

Method of Determining Inert Matter

Weigh out accurately about 1 g. of cement into a 4-inch platinum basin. Add 20 ml. concentrated hydrochloric acid, cover with a clock glass and place on a steam bath for three-quarters of an hour, stirring now and again. Then add 1-ml. of concentrated hydrochloric acid and continue heating and stirring for a quarter of an hour. Then dilute somewhat with hot water, add some ashless filter aid and stir to disperse it. Take the basin off the steam bath and filter the contents on a 12.5 cm. No. 40 Whatman (registered Trade Mark) filter paper. Wash out the basin into the filter. Wash the residue three times with hot water. Then wash the residue into a 250 ml. tall form beaker paying attention to the residue caught in the folds of the filter paper. Reserve the filter paper. 90 95 100

Make up the contents of the beaker to 100 ml. and place in a boiling water bath until at 100°C. Add 6 g. anhydrous sodium carbonate and stir frequently for 15 minutes. Add some ashless filter aid and filter on reserved filter. Wash three times with hot water, three times with hot 1-in-20 hydrochloric acid and then five times with hot water. Dry the filter nearly but not quite to dryness and ignite in a crucible at about 900°C to constant weight. Determine the weight of the ignited residue and express it as a percentage of the cement. 105 110 115

Analyse the residue for SiO₂, Al₂O₃, Fe₂O₃ and CaO by any suitable method well-known to competent analytical chemists. 120

This residue represents the inert material which plays no useful part in the setting and hardening process.

The water to be used in this test must be

either distilled or de-ionized water. The chemicals used are to be of analytical reagent quality. Porcelain basins and crucibles may be used but platinum is preferred.

5 WHAT WE CLAIM IS:—

1. A method of making a constructional cement which comprises (a) preparing a particulate chemical combination of oxides selected from (i) anorthite with excess silica in solid solution in the anorthite and (ii) anorthite with albite in an amount not more than 30 per cent by weight in solid solution in the anorthite, by sintering a mixture of minerals which together contribute the constituent oxides of the combination or of compounds which form said oxides under sintering conditions, in stoichiometric proportions to form said combination, whereby said oxides combine, and grinding the sintered product; and (b) reacting said ground product with an aqueous solution of orthophosphoric acid.

2. A method according to Claim 1, wherein said aqueous solution contains 35 to 75 per cent by weight of orthophosphoric acid based on the solution.

3. A method according to Claim 2, wherein said aqueous solution contains an amount of zinc orthophosphate not exceeding 15 per cent by weight based on the solution.

4. A method according to Claim 2, wherein said aqueous solution contains an amount of aluminium orthophosphate not exceeding 20 per cent by weight based on the solution.

5. A method according to Claim 1, 2, 3 or 4, wherein said combination of oxides is augmented by a compound having a retarding effect on the setting of the cement.

6. A method according to any preceding Claim which further comprises incorporating

in the cement composition an aggregate material to form concrete.

7. A method according to any preceding Claim which further comprises incorporating in the cement composition a fibrous material reinforcement.

8. A method according to any preceding Claim wherein said mixture contains Fe_2O_3 .

9. A method according to Claim 8 wherein the raw materials include a ferruginous clay.

10. A method according to Claim 8 or 9, wherein said mixture contains at least 10 per cent by weight of iron oxide and the sintering is carried out at a temperature not exceeding 1200°C .

11. A method according to any of Claims 1 to 7, wherein the sintering is carried out at a temperature of 1100°C to 1500°C to obtain maximum chemical combination of said selected oxides.

12. A method according to any preceding Claim wherein said mixture includes a flux.

13. A method according to any preceding Claim wherein said particulate combination has a characteristic particle size of at least 15 microns and contains 20 per cent by weight or more magnetite.

14. A method according to Claim 1 of making a cement composition which further comprises incorporating glass or silica fibre reinforcement.

15. A method according to Claim 1 of making a cement composition substantially as described with reference to the Examples.

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